

Process Resolution of Laser Sintering Process Using Plastic Powder Containing Inorganic Filler at a High Rate

Toshiki NIINO, Shunsuke OIZUMI and Kazuki SATO, Institute of Industrial Science,
The University of Tokyo, Japan
4-6-1 Komaba Meguro Tokyo, 153-8505 Japan
niino@iis.u-tokyo.ac.jp

ABSTRACT

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Research is being performed on a laser sintering process in which inorganic filler is employed as porogen at a high content to fabricate highly porous three dimensional tissue engineering scaffold. Previously, the scaffold, which included capillary like flow channel network, was used in cell culture test, but obtained cell density was limited due to insufficient fineness of the network structure. In the scaffold fabrication the author experienced degradation of process resolution when inorganic filler was introduced at a high content, but reasons for the low resolution has not been cleared. This paper investigates the dominating cause of the low resolution. Discussion is focused on effect of optical and thermal properties of filler. Experiments using transparent and opaque fillers are performed, and existence of dominating effect of difference in the optical property is denied. Experiments using thermally conductive solid filler and insulating hollow filler is performed, and it is concluded that temperature conductivity is dominating on process resolution.

INTRODUCTION

Difficulty of eliminating pores in laser sintered plastic parts is one of the most serious drawbacks with the process in the most industrial applications. Fore example, the inevitable porosity lowers the mechanical strength of the parts than when they were processed by injection molding of the same material. This difference lowers the value of plastic laser sintering as prototype fabrication. For another example, opaqueness due to the existance of pores is also limitting the use of the process both for rapid prototyping and rapid manufacturing. On the one hand, in other field than industrial production, there are several applications that rather require pores. Fabrication of three dimensional tissue engineering scaffold is one example, and the authors are developping laser sintering technology to fabrication of scaffolds that can be employed in regeneration of soft tissues such as livers.

A great amount of effort has been invested into establishment of regenerative medicine in the last several decades[1]. As a result, application to skins had been successfully

commercialized, and reconstruction of more three-dimensional bones and cartilage has become possible as far as experimental animal tests according to some reports[2]. Comparing to reconstruction of these tissues, on the other hand, that of soft tissues is much more difficult since most of these organs or tissues consume oxygen at such a high rate that cell culturing up to a thickness of more than some hundred microns causes necrosis. To provide all the cell in the scaffold with sufficient oxygen, a scaffold equipped with flow channel network had been proposed[3, 4]. The authors are developing a fabrication technology for such scaffold as an application of laser sintering freeform fabrication (Fig. 1). As mentioned above, a scaffold should include pores to provide the space in which cells are cultured, and the porosity should be more than 90%. Since

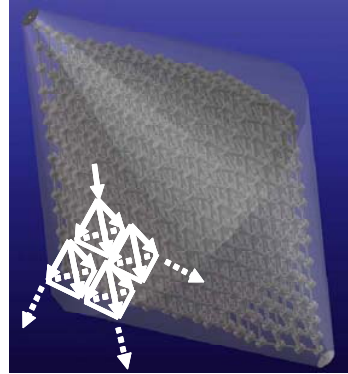


Fig. 1 Schematic of flow channel network

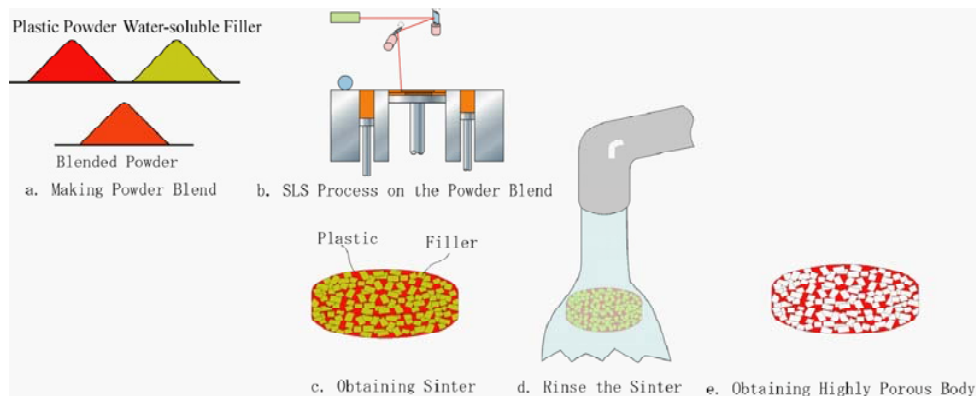


Fig. 2 Process For Fabricate Porous Object

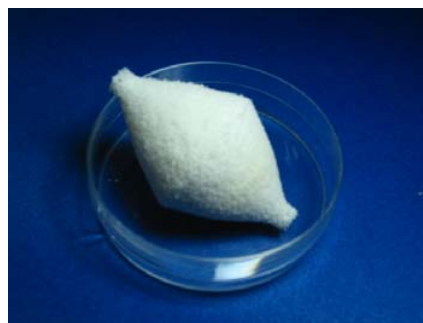


Fig. 3 Photo for Scaffold

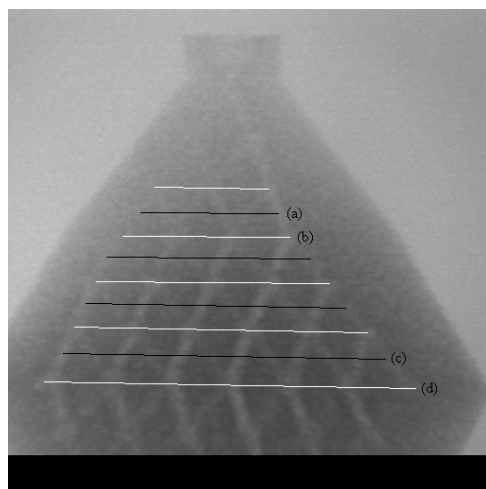


Fig. 4 X-ray photo for a scaffold

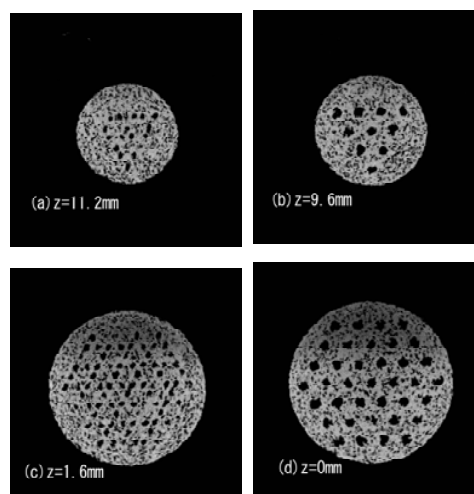


Fig.5 CT reconstructed cross section

this value cannot be obtained by normal laser sintering process, the authors are proposing a modified process in which water leachable filler is mixed with biodegradable plastic powder and leached out after sintering process is finished to improve porosity (Fig. 2). Formerly, we succeeded in fabricating a scaffold of polycaprolactone (Fig. 3). Owing to this porogen leaching process, the scaffold has a very high porosity of 90%. In the scaffold, flow channels of 1mm in diameter are repeating branching and joining to form a network that consists of a stack of tetrahedrons (Fig. 4, 5). Using this scaffold, cells that were originated from liver cancer were successfully cultured up to a cell density of one sixth of human liver.

Since the cells which are located away from the flow channel are provided with oxygen by diffusion, cell culture at high density can be performed only in the limited range from the channels. Thus, in order to culture the cell in the whole scaffold at a high rate, the size of the each tetrahedron that is formed by flow channel should be small. The prototype that the authors developed, was 4mm in the edge length of the tetrahedron, and cell density reached one sixeth of human liver as referred above. It is expected that the cell density could be improved by reducing the size of the tetrahedrons, but it was not realized by limited process resolution. Additionally, the authors experienced degradation of the resolution when inorganic porogen is introduced. In this paper, we investigate dominating cause of this degradation of process resolution.

EFFECT OF TRANSPARENCY OF INORGANIC FILLER

Laser sintering fabrication is composed of several procedures such as preheating, repetitive powder supply and laser exposure and cooling. Among them, laser exposure procedure plays most dominating role in deciding resolution of laser sintering

fabrication. Laser exposing procedure can be divided into four physical processes, laser absorption, temperature rise, sintering of grains, and temperature decrease by heat diffusion. Among these processes, the first two seem to affect process resolution the most significantly. In this section we discuss about change in laser absorption property by adding inorganic filler and its effect on process resolution.

Currently, most of commercially available plastic laser sintering machines employ CO₂ laser as their light sources. Wavelength of the CO₂ laser is approximately 10.6μm, and light with this wavelength is absorbed by most plastics at a very high rate. In the process of scaffold fabrication, sodium chloride is selected as the inorganic porogen from view point of nontoxicity. Contrary to plastics, sodium chloride rarely absorbs CO₂ laser (transmittance of NaCl crystal @ 10.6μm > 90%) [6]. Therefore, it is expected that the high transparency allows the laser scatter in the powder bed and increase the temperature of the powder in the wider range than when no filler is added. This might lead to increase of excessive sinter, which reduces the process resolution. In the following sections, several tests using various powder blends are reported and effect of high transmittance of CO₂ laser is discussed.

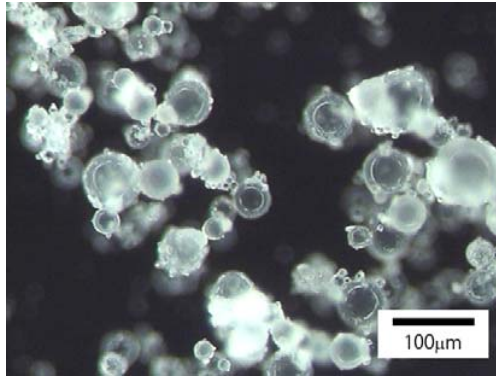
MEASUREMENT OF TRANSMITTANCE THROUGH POWDERS

As plastic powder, polycaprolactone (PCL), which was used for fabrication of scaffold in the author's laboratory, is employed. To this powder, sodium chloride and microsphere of soda-lime glass (GB731, Potters-Ballotini) is added. Soda-lime glass, which is completely opaque in contrast with NaCl, was used to evaluate the effect of the high transparency of sodium chloride. PCL and sodium chloride were sieved to limit the range of grain size. Micrographs and properties of the powders are shown in Fig.6 and Tbl. I.

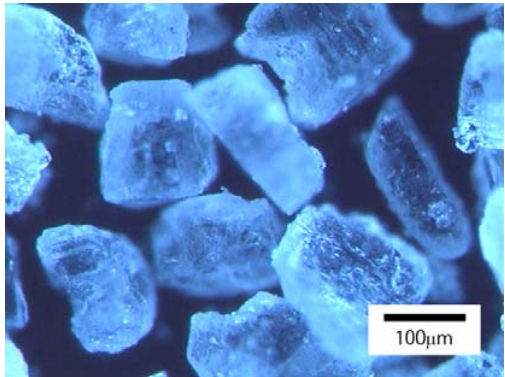
Measurement of transmittance of acrylic-styrene copolymer and its composite was reported by Cheung et al [7]. Since the material they tested or filler content of 30% in volume did not fit our purpose, we built a similar apparatus as shown in Fig. 7 and tested our materials by following their measurement method. A sheet of BaF₂, whose transmittance is around 90%, is placed above laser power meter (OPHIR, Type 3A) and specimen powder is coated on the sheet (window) so as to form a thin film. Thickness of the film, d_f was obtained by

$$d_f = \frac{m_f}{A \rho_b}$$

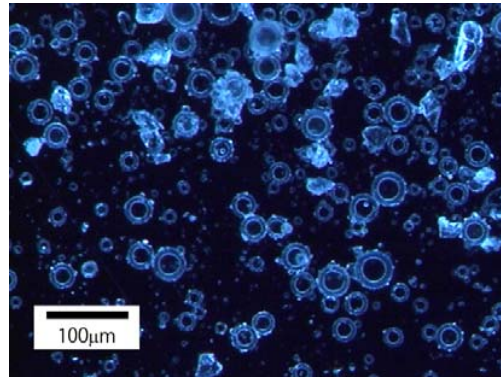
where m_f , A , and ρ_b are mass of the film (measured), area of film which is limited by a ring (Fig. 7) and bulk density of the powder. Transmittance was calculated by dividing laser power through the film by that without the film. Fig. 8 and 9 show relationship



(a) PCL



(b) Sodium Chloride



(c) Glass Microsphere

Fig. 6 Powder and Fillers

Tbl. I Properties of fillers (1)

	PCL	NaCl	Glass microsphere
Mean grain size [μm]	50	100-150	30
True density [kg/m^3]	1140	2160	2500

between transmittance and film thickness for PCL, sodium chloride (NaCl), glass microsphere (GB) and their composites. In the each composite, 200% in true volume of filler is added. It is found that sodium chloride increases the transmittance and glass microsphere decreases or almost eliminates it.

MEASUREMENT OF EXCESSIVE SINTER

To evaluate the effect of transmittance on process

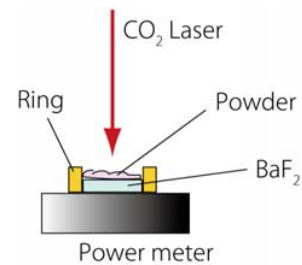


Fig. 7 Transmittance measurement apparatus

resolution, we used excessive sinter. A test piece as shown in Fig. 10 was fabricated, and error from the designed thickness is used as the excessive sinter. Parameters other than laser power are summarized in Tbl. II. Fig. 11 shows relationship between excessive sinter and laser power. Excessive sinter was increased by using sodium chloride. Excessive sinter of glass filled powder was also greater than of not filled version and even worse than when salt is added although transmittance was lowered. These results indicate that effect of transparency of filler on excessive sinter is rare or not dominant at least. We discuss about thermal property of filler as another potential factor that effect on the process resolution in the next section.

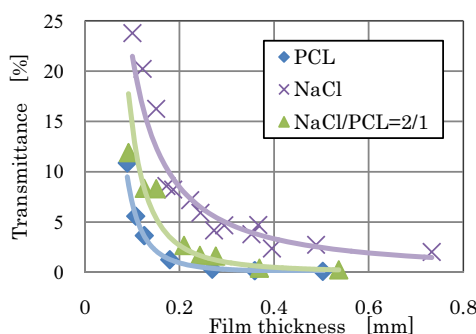


Fig. 8 Transmittance of NaCl added PCL

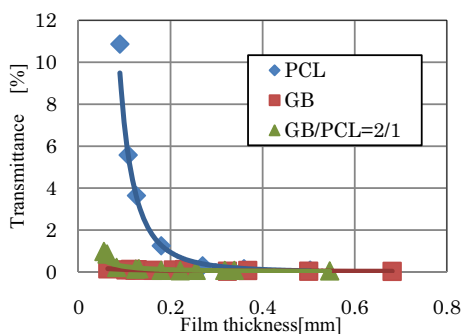


Fig. 9 Transmittance of GB added PCL

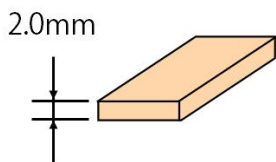


Fig. 10 Test piece for excessive sinter evaluation

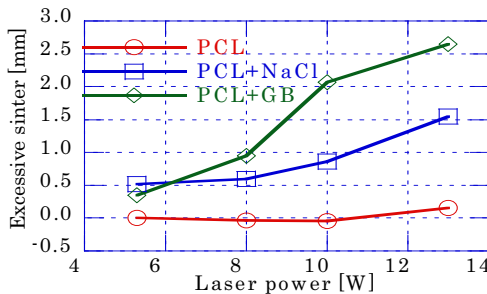


Fig. 11 Relationship between excessive sinter and laser power

Tbl. II Process parameters

Scan Speed	3.8m/s
Scan Spacing	0.1mm
Layer Thickness	0.2mm
Part Bed Temperature	50°C

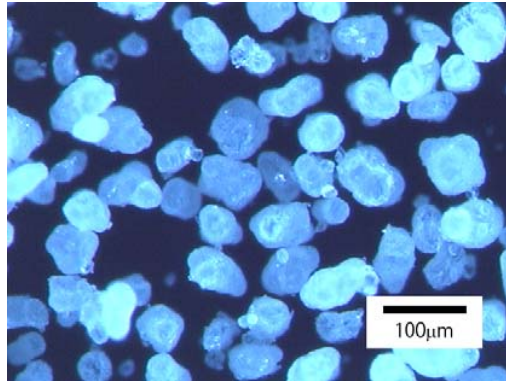
EFFECT OF THERMAL CONDUCTING PROPERTY OF INORGANIC FILLER

Another physical process that seems to give not negligible effect on process resolution is properties relating to thermal conduction in the powder bed. Generally, inorganic material conduct heat more than organic material. Therefore, we can guess that adding

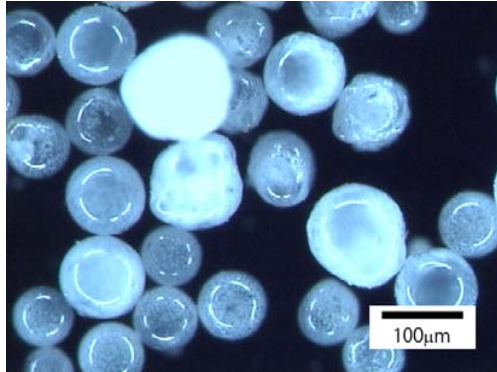
inorganic filler reduce temperature gradient around focal point of the laser and widens sintering area to reduce controllability of sintering area. In the following sections, several tests using various powder blends having different thermal property are reported and effect of difference in thermal conduction performance of filler on process resolution is discussed.

MEASUREMENT OF THERMAL CONDUCTIVITY OF POWDER BEDS

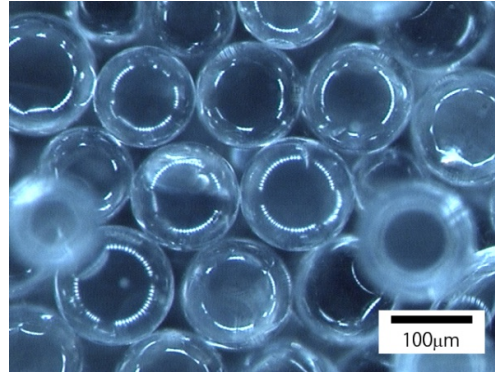
As plastic powder, polyamide 12 (DuraForm PA) is employed. To this powder solid



(a) PA12 (DF)



(b) Hollow glass microsphere (SLG)



(c) Solid glass microsphere (J-100)

Fig. 12 Micrographs of PA12 powder and glass microspheres

Tbl. III Properties of fillers

	DF	SLG	J-100
Center Diameter [μm]	58	120-130	106-150
Bulk Density [kg/m^3]	410	400	1510
True Density [kg/m^3]	1000	2500	2500
Thermal transmittance [$\text{W}/(\text{m} \cdot \text{K})$]	0.22~0.31 *	1.09	0.94
Heat capacitance per volume [$\text{kJ}/(\text{m}^3 \cdot \text{K})$]	673	312	1758

microsphere of soda-lime glass (J-100, Potters-Ballotini) and hollow microsphere of aluminosilicate glass (Extendosheres SLG, Potters-Ballotini) is added. Hollow glass microsphere is used to obtain low thermal conductivity. Micrographs and properties of the powders are shown in Fig.12 and Tbl III.

Thermal conductivity of powder bed was measured by using an experimental setup as shown in Fig. 13. In the powder, a thermocouple is located at a certain depth, and powder surface just above the thermocouple is shot by focused laser. The thermal conductivity, κ , is roughly estimated [8] by

$$\kappa = \frac{z^2 \rho c_p}{6t_{max}} \quad (1)$$

where z , ρ , c_p and t_{max} are depth of the thermocouple, density of the powder, specific heat and time that is spent for the temperature measured by the thermocouple to reach the maximum after laser shooting (Fig. 14). Fig. 15 illustrates thermal conductivities of PA12 (DF), solid glass microsphere (J-100), hollow glass microsphere (SLG), J-100 added DF (DF+J-100) and SLG added DF (DF+SLG). As shown here, solid glass microsphere's conductivity is much higher than that of PA12. Hollow glass microsphere has greater conductivity than PA12, but the difference is much smaller than between PA12 and solid glass microsphere. Adding solid glass microsphere increases thermal conductivity of powder by a factor of three while hollow one does by a factor of only 1.3.

MEASUREMENT OF SINTERING DEPTH

To evaluate effect of difference in thermal conductivity of powder on process resolution, sintering depth was measured in various conditions. Fig. 16 illustrates relationship between sintering depth and supplied laser energy per unit area. As shown here, sintering depth at the same energy supply is smaller in the case that hollow glass microsphere is added although thermal conductivity is lowered. This means that thermal conductivity is not adequate index to show how easily sintering area spreads. Since sintering happens when the temperature exceed a certain value such as melting temperature, we should not consider how easily heat diffuse but how easily high temperature area is spreading. Since unsteady state, one dimensional, energy balance is given by,

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right) + G(z, t) \quad (2)$$

where T is temperature, t is time, z is depth, and $G(z, t)$ represents the heat sink due to compositional change such as polymer decomposition, we should adopt thermal diffusivity (or temperature conductivity) α , which is defined as,

$$\alpha = \frac{\kappa}{\rho c_p} \quad (3)$$

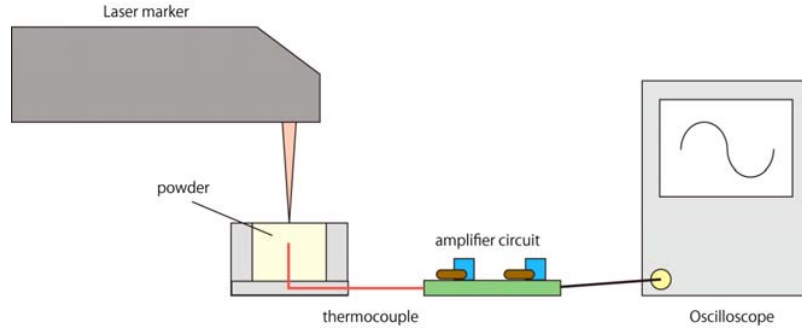


Fig. 13 Measurement setup for thermal conductivity

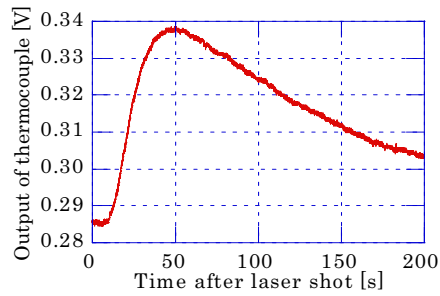


Fig. 14 Output of thermocouple

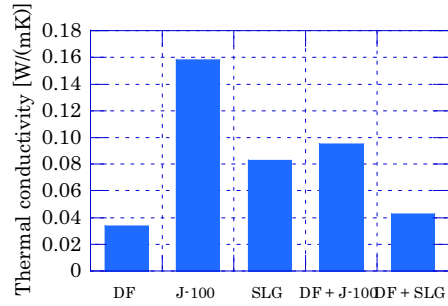


Fig. 15 Thermal conductivities

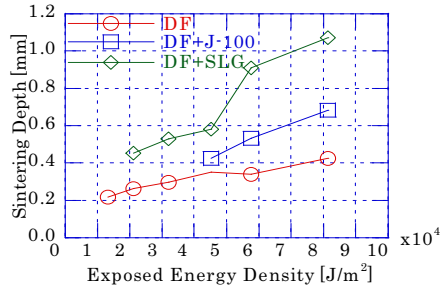


Fig. 16 Relationship between sintering depth and energy

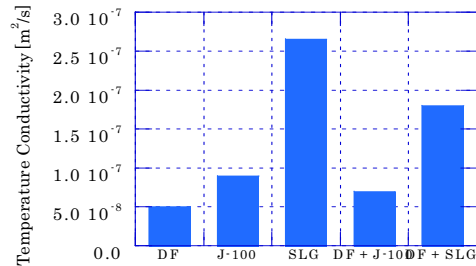


Fig. 17 Temperature conductivities

Fig. 17 illustrates temperature conductivities of powders. Here, the order of temperature conductivities of the powders using the two filler agrees with the result of sintering depth measurements. This indicates that temperature conductivity is dominating factor of deciding process resolution.

DISCUSSION

Though we could not find any evidence that transparency of filler reduces process resolution, it is not reasonable to conclude there is no effect. It is true that the optical effect is smaller than thermal effect. In addition, since it is easier to reduce

transparency by adding dyes or pigments than to improve, transparency cannot be serious obstacle to improve process resolution. Contrary, problem of thermal property is more serious. Since it is difficult to decrease thermal conductivity without decreasing heat capacitance by only changing shape of filler, we have to find another material that possesses better nature. Though we did not discuss about effect of heat sink term in this paper, effect of this term must be investigated in the future.

In this paper we regarded the powder beds which consist of plastic powders, high content inorganic fillers, and air as continuum, and measured their transparencies and thermal conductivity. We discuss about relationship between amount of excessive sinter or sintering depth as indices of process resolution and the measured optical and thermal properties. Relationship between these properties of the powder beds and those of the components were discussed only qualitatively. We have to investigate the relationship in more quantitative way by regarding the beds as non-continuum to find a better recipe for precise fabrication of highly porous body.

CONCLUSION

To improve process resolution of laser sintering freeform fabrication using a large amount of inorganic filler, effects of high transparency and thermal conductivity of the filler are investigated. On the supposition that use of transparent filler enhances scattering of CO₂ laser and lower the process resolution, we tested transparent and opaque filler and compare the amount of excessive sinter. As a result, we did not find significant difference. To investigate, relationship between thermal conductivity and process resolution, solid and hollow glass microspheres are used as filler and sintering depth was measured. The heat equation suggests that temperature conductivity has more direct relation with spread of sintering area, and the experimental results support this. Therefore, we can conclude that temperature conductivity is important index for prediction of process resolution. To improve process resolution of laser sintering fabrication using high content filler, we have to find good material that has low thermal conductivity and high specific heat in its nature.

References

- [1] Wai-Yee Yeong, *et al*: Rapid prototyping in tissue engineering: challenges and potential; TRENDS in Biotechnology Vol.22No.12 December2004
- [2] Suman Das Scott F. Hollister *et al*; Freeform fabrication of Nylon-6 tissue engineering scaffolds, Rapid Prototyping Journal Vol.9, Number1, 2003, pp.43-49
- [3] Y. Sakai, *et al*: A novel poly-L-lactic acid scaffold that possesses a macroporous

structure and a branching/joining three-dimensional flow channel network: its fabrication and application to perfusion culture of human hepatoma Hep G2 cells; Materials Science and Engineering C 24 (2004) 379–386

[4] Kim SS, Utsunomiya H, Koski JA, Wu BM, Cima MJ, Sohn J, Mukai K, Griffith LG, and Vacanti JP: Survival and function of hepatocytes on a novel three-dimensional synthetic biodegradable polymer scaffold with an intrinsic network of channels. Ann Surg 228: 8-13 (1998)

[5] Niino T, SAKAI Y, HUANG H and NARUKE H: SLS Fabrication of Highly Porous Model Including Fine Flow Channel Network Aiming at Regeneration of Highly Metabolic Organs, Proc. Solid Freeform Fabrication Symposium 2006, 160-170, (2006)

[6] <http://www.korth.de/transmiss/nacl.htm>

[7] Fan K, Wong K and Cheung W, “Reflectance and transmittance of TrueForm™ powder and its composites to CO₂ laser”, Rapid Prototyping Journal, Vol.13, No.3, pp.175-181, 2007

[8] Furumoto T, Ueda R, Hosokawa A, Abe S, CHILDS T: Study on the Measurement of Physical Properties in the Metal Powder for Rapid Prototyping –Proposal of the Measurement of Thermal Conductivity and Absorption of Laser Beam, Journal of the Japan Society for Precision Engineering, Vol.73, No.5, pp.558-562, 2007 (in Japanese)